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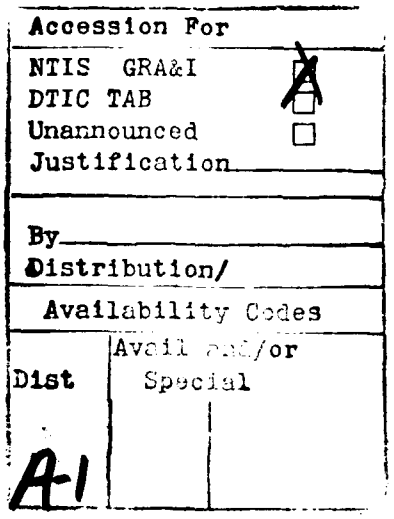

The Fabrication and Characteristics of Ta_2N Field Emitters

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Abstract: Tantalum nitride field emitters are fabricated by nitrifying a tantalum tip which give an electron emission current of 210μA at the tip voltage of 6.8kV and the temperature of 1300C, with a brightness of $3x10^3 A/cm^2$-str and an angular current density of $5x10^3$μA/str. The current fluctuation is small at a pressure of 10^{-8}torr, with a typical fluctuation smaller than 2.5% in 30 minutes. Typical field emission patterns are presented with a dark region at the center and two symmetrical bright regions on both sides. The composition of tip surfaces is analyzed by a scanning Auger microprobe.

I. Introduction

The electron beam emission elements used in micro-manufacturing are made more and more important with the rapid advancement of electronic components and devices. Furthermore, the development of scanning electron microscopes with high resolution also promote the study of high intensity electron beam sources.

At present, the mechanism of field emission of tungsten has been studied extensively and the results have been applied to many practical situations. However, the work function of tungsten is relatively high and due to the adsorption and decomposition of residual gas atoms and molecules on the surface, the diffusion of these adsorbed atoms and molecules, and the impact on the surface of the cathode from the positive ions produced by the ionization of the gas molecules, the emission current was in general very

unstable. In order to keep the current stable. it is necessary to operate the emitter under a vacuum of 10^{-10}torr or better. This is the reason why the tungsten field emitter cathode has not be used extensively. Therefore, the investigation of a new electron beam source with properties better than tungsten is important.

The material requirements for a good field emitter cathode are: high melting point, low vapor pressure under the working temperature, high mechanical strength, difficulty for the adsorption of gas molecules on its surface. low sputtering, and low work function. So far the materials under investigation are various carbides and borides and the use of nitrides in the manufacturing of field emitters has not been reported. The reason is that the melting point of nitrides are generally high and the growth of single crystal is difficult. Moreover, even if the single crystal nitride can be manufactured into the shape of cylinder or thread. due to its hardness and brittleness the subsequent forming process will be difficult and the electrical and thermal conductivity between the emitter and the supporter will also likely to be a problem. The difficulties mentioned above were overcome by special techniques developed in this work and the manufacturing of tantalum nitride cathode was achieved. In the following we will report some of the major achievements.

II. Manufacturing and Characterization of Tantalum Nitride Emitter Cathode

The method used in this work did not require the single crystal tantalum nitride for the manufacturing of the emitter cathode tip. Instead, the manufacturing of the emitter tip was done by nitrifying of a tantalum tip. The manufacturing process is summarized below:

First the tantalum thread is electrolytically corroded (the electrolyte is the mixture of HF, H_2SO_4, H_3PO_4, CH_3COOH and water) to make a needle tip of 10^{3}Å in diameter and with a height less than 0.1um. At this moment, the tip is not smooth and is polycrystalline, and the surface of the tip is not clean. Therefore, when high voltage is applied to the cathode (in vacuo), the field emission pattern will not appear.

Secondly, the tantalum tip will be placed in the ultra-high vacuum system for purification and tempering treatment. The treatment will continue until the typical tantalum field emission pattern with two symmetrically lighted spots appears. This is an indication that the tip is smooth and rounded; due to the migration of tantalum atoms during the treatment process, the single crystal is formed, and the surface is cleaned.

Finally, the tip will be heated to about 1600 - 2000°C (under the environment of the mixture of high purity nitrogen and hydrogen: N_2 partial pressure is 7.5torr and H_2 partial pressure is 160torr) for nitrifying for one minute. This is the preform of the emitter cathode with tantalum nitride at the tip.

When the emitter tip is observed with optical microscopes, the "tip" image can only be seen very vaguely and the detailed geometric pattern can not be obtained. We have observed the secondary electron images of more than 20 tantalum nitride emitters, which we have measured before, using the Lionix ESM-302 scanning electron microscope. One of the "tip" image is shown in figure 1. Even though the tips all have different dimensions and shapes, most of the "tips" do not have a pointed head but rather a very smooth surface.

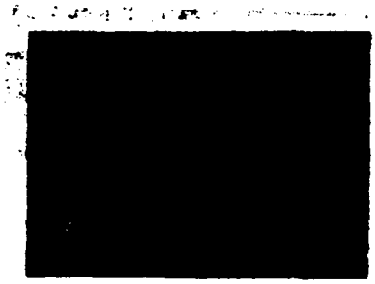

Figure 1: The "tip" image of a tantalum nitride field emitter by the scanning electron microscopy.

The substrate used in the "nitrifying" method is tantalum thread. Therefore the manufacturing and forming are relatively easy. The electrical and thermal contact between the tantalum nitride and the supporting tantalum thread is very good, and this contact property can still be preserved even under high temperature conditions. During nitrifying process, the nitrogen gas was not introduced,[1] and this was to avoid the contamination of the system.

III. Experimental Equipment and Measuring Technique

The vacuum chamber used for field emission experiment consisted of the mechanical pump, the turbo molecular pump, the ionic pump, and the titanium sublimation pump cooled by liquid nitrogen. The ultimate vacuum achievable is on the order of 10^{-10}torr. An anode plate with 80mm in diameter was instaled about 25mm away from the tantalum nitride emitter. A hole of 0.2mm in diameter was opened up in the center of the anode plate. On the other side of the hole were a secondary electron restraining electrical pole and a Faraday tube. The Faraday tube was used to collect the electron stream that passed through the anode. This part of the current was called the probing current I_p and the electron beam current collected by the anode was called the total current I_t. A glass luminescence screen was installed in the vacuum chamber so that the field emission pattern can be photographed through the vacuum chamber. The cathode tip temperature was measured by the infrared thermometer (Japan Minolta type IR-630).

One of the important indicators of the electron source is its brightness. The brightness at an angle 0 from the normal direction of the emitter is

$$B=\frac{\Delta I}{\Delta S\cdot\Delta\omega\cdot\cos\theta} \qquad (1)$$

where ΔI is the equivalent current density emitted by the electron source within the Δw solid angle and at the θ angle from the normal direction. In the experiment, $\Delta I = I_p$. $\Delta S = \pi r^2$ is the equivalent electron emission area and r is the radius of the equivalent electron source.

IV. Experimental Results and Discussion

1. The Emission Pattern of Tantalum Nitride Emitter

The initial field emission pattern of the tip after the nitrifying treatment is shown in figure 2. The tip temperature was below 1400°C and the emission current was about 10^{-6} - 10^{-5}Å. The center of the emission pattern is a dark region and two bright regions located symmetrically on both sides of the dark region. At the center of the bright regions are a few smaller dark regions. Each of these dark regions corresponds to one of the particularly oriented crystal plane with less emission. In other words, these dark regions correspond to the crystal planes with higher work functions.

If high voltage is applied and if the tip temperature is increased to above 1400C in a short time, then the emission current increased to 10^{-4}Å rapidly and the field emission pattern is shown in figure 3. The basic features of figure 3 are the same as those of figure 2, however, the smaller dark regions in the center disappear and are replaced by bright spots, with brightness even higher than the surroundings. In other words, the work function of these crystal planes changed from a higher value to a lower value. It is worth mentioning that under this condition the brightness of the originally bright region do not change. This is different from the "molding" process often occurred with the tungsten field emitters. After "remolding" operation of the tungsten emitters, some of the dark

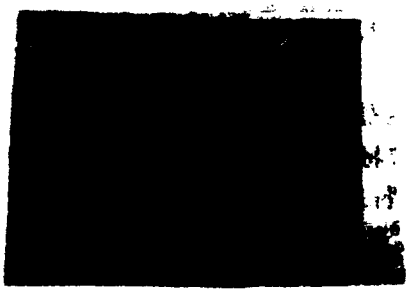

Figure 2: The field emission pattern of tantalum nitride at low emission current state.

Figure 3: The field emission pattern of tantalum nitride at high emission current state.

regions in the tungsten emission patterns will be transformed into bright regions and, at the same time, some of the bright regions will be transformed into dark regions.[2] We did not observe any of these phenomena in our experiments.

The high emission state can only be maintained under the condition of high temperature and high field strength. When the tip temperature dropped to below 1250°C or if the voltage is decreased, then the field emission will be transformed back to the condition in figure 2. Under the condition of high field strength, if the tip temperature is increased, not only can electrons obtain more energy, the surface atom migration will be promoted as well. These atoms will migrate towards certain crystal planes and result in the enhanced emission from these planes. This is the cause for the high emission current.

According to the geometrical theory of crystal structure and the symmetries in figures 2 and 3, the crystal structure at the tip was determined to be cubic structure.

If the temperature it too low during the nitrifying process of the tantalum tip, and if the partial pressures of water vapor and oxygen in the residual gas of the vacuum system are low, then the hexagonally symmetrical emission patterns (see figure 4) will appear. The emission current can be as high as 70 micro-A. However, even under this condition, if the tip temperature is increased without increasing the applied voltage, the emission pattern can be transformed into figures 2 or 3. On the contrary, if the tip temperature is lowered, the transformation of the emission patterns from the binary-symmetrical pattern to the hexagonally-symmetrical pattern has never been observed. Therefore, it can be concluded that when the temperature is increased, a "recrystallization" process will occur and

Figure 4: The hexagonally symmetrical emission pattern of tantalum nitride emitter.

the crystal structure corresponds to the binary-symmetrical emission pattern is a stable state with respect to that temperature.

2. Thermal Field Emission (TFE) Current and Its Stability

When the vacuum level reached $6x10^{-8}$torr, the voltage applied to the tantalum nitride tip was 6.8kV, and the tip temperature was 1300°C, the thermal field emission total current I_t was about 210μA and was stable. According to the measurement of I_p and the calculation based on equation (1), the brightness at the center of the bright region was $3x10^8$A/cm^2-str and the angular current density was $5x10^3$μA/str.

Figure 5 shows the measurement results of the variation of I_t and I_p with time. Similar to the cases of TiC[3] and TaC,[4] pulse-like current-drops occurred. However, different from the case of TiC, the variation in I_t and I_p occurred simultaneously. In other words, the local current change is consistent with the total current change for tantalum nitride.

The change in field current is caused by: adsorption and decomposition of residual gas atoms; surface diffusion of adsorbed atoms; and impact on the emitter surface by the positive ions of the residual gas atoms. Comparing with the tungsten emitters, the adsorption of residual gas atoms onto the surface of semiconductor emitter is relatively difficult. Moreover, even if adsorption occurs, the variation in emission current is less.[5] Even under a vacuum of 10^{-8}torr, tantalum nitride can still provide more stable emission. The pulse-like current change was mainly due to the impact on the emitter surface caused by positive ions. If the pulse-like current change is not considered, the noise of the thermal field emission current is less than 3% and the drift in field current in 30 minutes in less than 2.5%. Therefore, better field emission characteristics can be obtained with the tantalum nitride emitters.

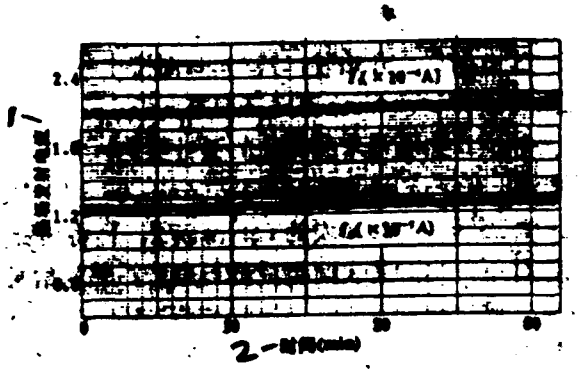

Figure 5: The time-variation of I_t and I_p.

key: 1 - thermal field emission current
2 - time (min)

We have also investigated the relationship between current I_t and the applied voltage V at a tip temperature of 1290°C. The results are shown in figure 6. Under the conditions when the field current is small, the emission of tantalum nitride and metallic emitters are similar; both obey the Fowler-Nordheim equation; namely, linear relationship exists between $\log I_t/V^2$ and 1/V. From the slope of this straight line, the work function of tantalum nitride was found to be about 3.84eV. Under the condition when the field current is large, the experimental curve deviated from the F-N equation and became non-linear. It can not be determined whether this was due to the effect of space charges or the semiconducting characteristics of tantalum nitride that transport of electron towards the surface is approaching saturation.

The tantalum nitride tip manufactured in this work can be exposed to atmosphere. We have exposed a tantalum nitride tip in the atmosphere for three months. After the exposure the tip was put back in the vacuum chamber. After heating and de-gassing treatments, the field emission characteristics remained unchanged.

3. Auger Analysis of the Cathode Surface

The tantalum nitride emitter which was capable of generating the emission pattern was analyzed in the AAS-200 Auger spectrometer (manufactured by Anelva) to characterize the nitrified layer on the surface. In order to keep the surface clean, when the analysis was performed, the hydrogen ion gun was used to impact and peel the surface of the cathode. In the beginning, the element peaks in the Auger spectrum varied with time. After about one hour, the height of Auger current spectrum peaks corresponding to various elements approached a steady state. The result is shown in figure 7.

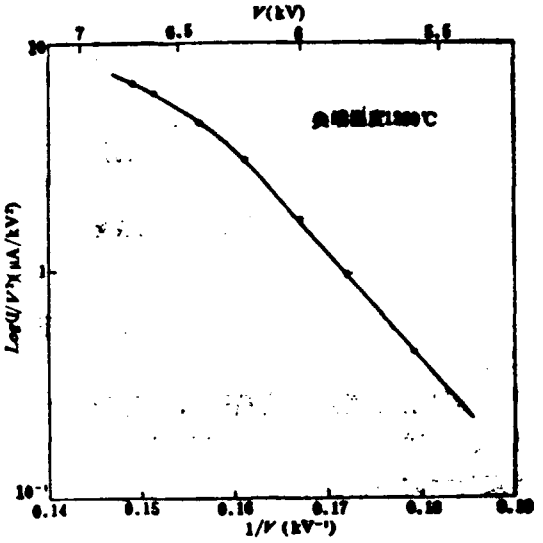

Figure 6: The relationship between $\log I/V^2$ and $1/V$ at a tip temperature of 1290C.

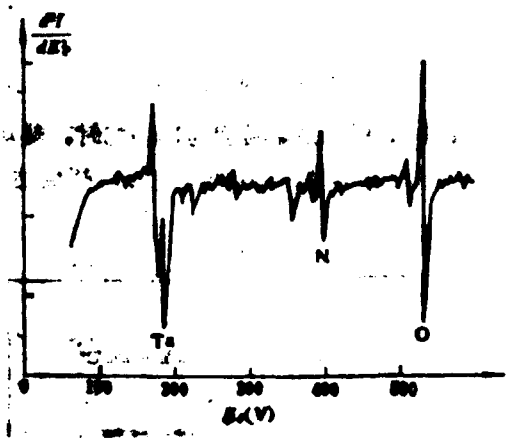

Figure 7: The Auger peak of tantalum nitride manufactured by nitrifying technology.

On the other hand, we have also placed a tantalum tip, without nitrifying treatment, in the SPC-530H high frequency planar magnetically-controlled sputtering system (manufactured by Anelva). Under the condition of high frequency, 3kW of power, $5x10^{-4}$torr of nitrogen partial pressure, and $2x10^{-3}$torr of hydrogen partial pressure, a layer of TaN thin film, with a thickness of 2000Å,[6] was condensated on its surface. This tip was also analyzed with the Auger spectrometer. Under identical conditions, the surface composition was also analyzed and the result in shown in figure 8.

The peak-to-peak magnitude ratio of nitrogen peak and tantalum peak and the shape of the tantalum peak in figure 7 are different from those in figure 8. Therefore, the structure and composition of the tantalum nitride manufactured by the nitrifying method are different from the cubic TaN manufactured by the sputtering method.

From the presently available data,[7-9] there are thirteen different compositions and structures of tantalum nitride. Table 1 shows their parameters. According to table 1 and from the symmetry shown in the field emission pattern, the tantalum nitride manufactured by the nitrifying method is most likely the cubic Ta_2N.

V. Comparison and Conclusion

From the basic characteristics of the tantalum nitride thermal field emitter mentioned above, the use of this compound as a new point-electron-source is promising.

Comparing with tungsten, tantalum nitride has lower work function, lower working temperature, higher angular current density, and was less affected by the residual gas atoms. Therefore, it can be used in a vacuum which is two order of magnitude lower than what tungsten requires (and still provide

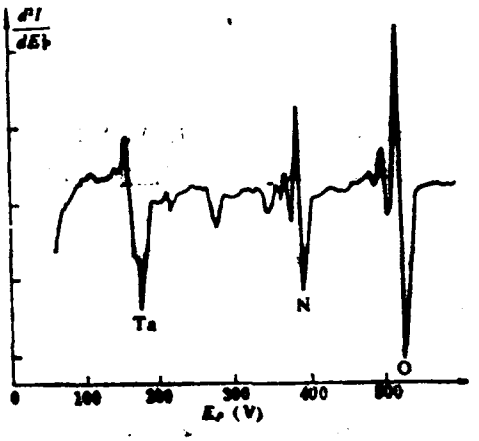

Figure 8: The Auger peak of tantalum nitride manufactured by the reaction sputtering technology.

Table 1

compound	unit crystal	space group	structure	a(Å)	c(Å)	c/a
TaN	cubic	O^5_h-Fm3m	NaCl	4.344		
TaN	hexagonal	D^1_{3h}-P6m2	WC	2.933	2.864	0.98
TaN	hexagonal	D^1_{6h}-P6/mmm	CoSn	5.183	2.907	0.56
Ta_2N	cubic			10.09		
Ta_2N	hexagonal	C^4_{6v}-$P6_3mc$	ZnS	3.042	4.909	1.61
Ta_5N_6	hexagonal	D^3_{6h}-$P6_3/mcm$		5.213	10.426	2.0
Ta_4N_5	square	C^5_{4h}-I4/m		6.840	4.241	0.62
Ta_3N_5	square			10.252	3.896	0.38
$TaN_{0.83}$	hexagonal	$P\bar{6}m2$		2.925	2.876	0.98
$TaN_{0.80}$	hexagonal	P6/mmm		2.931	2.879	0.98
gamma-$TaN_{0.4}$	hexagonal			3.040	4.907	1.61
gamma-$TaN_{0.45}$	hexagonal			3.048	4.918	1.61
beta-$TaN_{0.1}$	cubic			3.369		

the same brightness). Comparing with tantalum,[4] the nitrifying technique is simple, the success rate is high, and the nitrifying temperature is less than the carburization temperature which is above 2300°C. It is not necessary to introduce the gas which may contaminate the vacuum system (such as C_2H_4, ... etc) during nitrifying. After nitrifying, it is not required to introduce oxygen for decarburization treatment. Besides, the emission characteristics of these two emitters are very similar.

More work is required to understand the mechanism of the formation of the pulse-like current and the ways to overcome it, the electron energy distribution, and the ways of estimating the service life of the emitter cathode.

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